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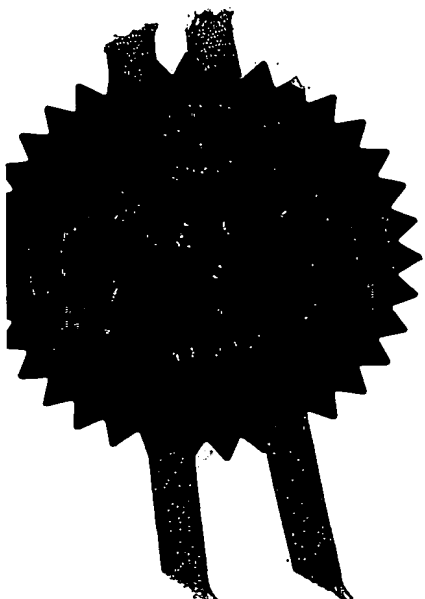
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Signed *AmBrewer*

Dated 7 February 2003

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GB 0201461.1

By virtue of a direction given under Section 30 of the Patents Act 1977, the application is proceeding in the name of

JOHNSON MATTHEY PLC,  
2-4 Cockspur Street,  
Trafalgar Square,  
LONDON,  
SW1Y 5BQ,  
United Kingdom

Incorporated in the United Kingdom

[ADP No. 08519803001]

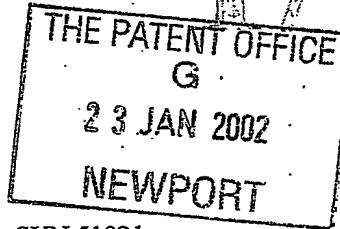
Patents Form 1/77

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# **Request for grant of a patent**

(see the notes on the back of this form. You can also get an explanatory leaflet from the Patent office to help you fill in this form)



The Patent Office

Cardiff Road  
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Gwent NP9 1RH

SYN 51021

**0201461.1**

1 Your reference

2 Patent application number  
(The Patent Office will fill in this part)

3 Full name, address and postcode of the or of each applicant (underline all surnames)

IMPERIAL CHEMICAL INDUSTRIES PLC  
Imperial Chemical House  
Millbank, London SW1P 3JF

Patents ADP Number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

9350037  
United Kingdom

4 Title of the invention

SULPHUR REMOVAL

5 Name of Your Agent (if you have one)

GRATWICK, Christopher

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Synetix Intellectual Property Department  
PO Box 1, Room N101  
Belasis Avenue  
Billingham  
Cleveland  
England, TS23 1LB

Patents ADP Number (if you know it)

7962249001

6 If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or each of these earlier applications and (if you know it) the or each application number

Country	Priority Application number (if you know it)	Date of Filing (day / month / year)
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7 If this application is divided or otherwise derived from an earlier UK application, give the number and filing date of the earlier application

Number of earlier application	Date of Filing (day / month / year)
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8 Is a statement of inventorship and of right to grant of a patent required in support of this request?

Yes

Answer yes if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See Note (d)

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Continuation sheets of this form	-
Description	4
Claim(s)	1
Abstract	1
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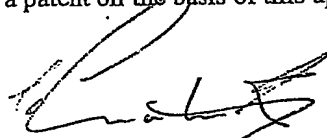
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Priority documents	
Translations of priority documents	
Statement of Invention and right to grant of a patent ( <i>Patents Form 7/77</i> )	
Request for Preliminary Examination and search ( <i>Patents Form 9/77</i> )	
Request for Substantive Examination ( <i>Patents Form 10/77</i> )	
Any other documents ( <i>Please specify</i> )	

11

I/We request the grant of a patent on the basis of this application

Signature



Date

22.01.2002

- 12 Name and daytime telephone number of person to contact in the United Kingdom

CHRISTOPHER GRATWICK  
01642 523860

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### Sulphur removal.

This invention relates to sulphur removal and in particular to the removal of elemental sulphur from gaseous or liquid hydrocarbons, e.g. gasoline.

5 Elemental sulphur may be present as a contaminant in liquid hydrocarbons. One source of such contamination is as a result of the transport of hydrocarbon via pipelines. In some cases batches of different hydrocarbons are pumped along a pipeline in sequence and as a result "clean" hydrocarbons such as gasoline may be contaminated by materials such as hydrogen sulphide from the previous use of the pipeline for a "dirty" hydrocarbon such as kerosene. Pipeline scale and/or ingress of small amounts of air can cause the oxidation of  
10 contaminants such as hydrogen sulphide to elemental sulphur. Sublimation of elemental sulphur may also result in contamination of gaseous hydrocarbons.

Removal of such elemental sulphur is desirable. We have found that certain ion exchange resins can absorb significant amounts of elemental sulphur.

Accordingly the present invention provides a method for the removal of elemental  
15 sulphur from a liquid hydrocarbon feedstock comprising passing the feedstock through a bed of an ion exchange resin containing primary or secondary amino groups.

The absorption may be effected at temperatures in the range  $-10^{\circ}\text{C}$  to  $+100^{\circ}\text{C}$  and preferably under sufficient pressure that the hydrocarbon is in the liquid or "dense phase" state, at the desired absorption temperature. By the term "dense phase" we mean that the  
20 hydrocarbon is at a pressure that is above the upper dew point curve and at a temperature above the critical temperature (but generally below the temperature of the maxcondentherm point - which is the maximum temperature of the dew point and bubble point curves).

Amine-containing ion exchange resins as supplied often contain a significant amount of water. We have found that such water can retard the absorption of elemental sulphur.  
25 Accordingly it is preferred that the ion exchange resin is dried, e.g. by extraction with a suitable solvent such as methanol, before use. The ion exchange resin, of which Amberlyst A.21 is a typical example, is preferably employed in the form of a fixed bed of shaped units, e.g. spherical granules, preferably having maximum and minimum dimensions in the range 0.5 to 10 mm.

30 In addition to absorbing the elemental sulphur, the ion exchange resin may catalyse the decomposition of elemental sulphur species such as the cyclic  $\text{S}_8$  species, forming polysulphides and hydrogen sulphide. Consequently it may be desirable to pass the feedstock through a bed of a suitable hydrogen sulphide absorbent after passage through the bed of the ion exchange resin. Suitable hydrogen sulphide absorbents include zinc and copper  
35 compounds such as oxides, hydroxides and basic carbonates. A particularly suitable absorbent that is effective at the temperatures mentioned above comprises agglomerates of co-precipitated copper, zinc and aluminium compounds and may contain a suitable binder, e.g. a calcium aluminate cement.

The ion exchange resin can be regenerated by periodic treatment with a suitable acid such as hydrochloric acid. However under favourable conditions, the ion exchange resin may have the capacity to absorb a sufficient amount of sulphur that it is economic to replace the resin when laden with the absorbed sulphur rather than to provide for regeneration.

5 Hydrocarbons that may be treated include any that are liquid under the operating conditions. Preferred hydrocarbons include natural gas liquids and gasoline.

The invention is illustrated by the following examples.

#### Example 1

10 A stirred vessel was charged with 200 ml of toluene in which about 10 mg of sulphur had been dissolved at room temperature. 5 g of an ion exchange resin, Amberlyst A.21 which contains methylamine groups, in the form of spherical granules of diameter about 1.5 mm was added to the vessel and stirring continued. Samples of the solution were taken for analysis at intervals. As no significant reduction in the sulphur content after 165 minutes, a further 5 g of the ion exchange resin was added and stirring, and intermittent sampling, continued for a  
15 further 3 hours. Stirring was then stopped and the vessel left to stand for 7 days. The sulphur content of the solution is shown in the Table 1.

Table 1

Time	Total sulphur content (mg/l)
0 min	45.5
10 min	46.1
30 min	46.1
165 min	44.1
210 min	34.3
300 min	18.2
345 min	8.3
7 days	0

It is seen that the sulphur was only absorbed slowly.

#### Example 2

20 The procedure of example 1 was repeated without the addition of the second 5 g of ion exchange resin and the vessel was left to stand for 3 days. The results are shown in Table 2.

Table 2

Time	Total sulphur content (mg/l)
0 min	44.1
30 min	43.2
60 min	44.0
180 min	40.7
240 min	35.8
315 min	23.0
360 min	14.5
3 days	3.5

Example 3

Analysis of the Amberlyst A 21 ion exchange resin as used in Examples 1 and 2 revealed that its initial water content was about 50% by weight. In order to reduce the water content, 10 g of the Amberlyst A21 resin was extracted in a separating funnel with two 50 ml aliquots of methanol. The methanol was then drained off and the resin dried in a stream of nitrogen. The procedure of Example 2 was then repeated using the extracted resin and a solution of 13 mg of sulphur in 200 ml of toluene. The results are shown in Table 3.

Table 3

Time (min)	Total sulphur content (mg/l)
0	44.5
30	37.0
90	0.04
220	0

It is seen that the sulphur was rapidly absorbed.

Example 4

To assess the capacity of the Amberlyst A 21 ion exchange resin for sulphur, 5 g of the resin was added to a solution of 2527 mg of sulphur in 200 ml of toluene. Samples of the resin

were removed at intervals, air dried and then analysed for total sulphur. The results are shown in Table 4.

Table 4

Time (hours)	sulphur content (mg/cm <sup>3</sup> )
5.5	14
7	19
24	41
51	51



Claims

1. A method for the removal of elemental sulphur from a hydrocarbon feedstock comprising passing the feedstock through a bed of an ion exchange resin containing primary or secondary amino groups.
2. A method according to claim 1 wherein the feedstock is contacted with the ion exchange resin bed at temperatures in the range  $-10^{\circ}\text{C}$  to  $+100^{\circ}\text{C}$  under sufficient pressure that the hydrocarbon is in the liquid or "dense phase".
3. A method according to claim 1 or claim 2 wherein water is removed from the ion exchange resin before use.
4. A method according to any one of claims 1 to 3 wherein the ion exchange resin is in the form of a fixed bed of shaped units having maximum and minimum dimensions in the range 0.5 to 10 mm.
5. A method according to any one of claims 1 to 4 wherein the feedstock is passed through a bed of a hydrogen sulphide absorbent after passage through the bed of the ion exchange resin.
6. A method according to any one of claims 1 to 5 wherein the ion exchange resin is periodically regenerated by treatment with an acid.

Abstract

Removal of elemental sulphur from a hydrocarbon feedstock by passage through a bed of an ion exchange resin containing primary or secondary amino groups.

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